A New 2D Zinc(II)-Organic Framework with Dinuclear Units Based on Iodinated Terephthalate: Synthesis, Crystal Structure and Luminescence Behavior

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A new coordination polymer $[Zn(BDC-I_2)(DMF)]_n$ (**1**) has been prepared by solvothermal reaction of Zn(II) nitrate with 2,5-diiodo-1,4-benzenedicarboxylic acid (H_2BDC-I_2) in ethanol-DMF, and characterized by elemental analysis, IR spectroscopy and single-crystal and powder X-ray diffraction techniques. Complex **1** shows a two-dimensional network possessing dinuclear $Zn_2(CO_2)_4$ secondary building units, which are further assembled into a three-dimensional supramolecular structure through intermolecular C–H···I interactions. Solid-state properties such as photoluminescence and thermal stability of **1** have also been investigated.

Key words: Iodinated Terephthalate, Zn(II)-Organic Framework, Solvothermal Synthesis, Crystal Structure, Luminescence

Introduction

Design and synthesis of coordination polymers, also known as metal-organic frameworks (MOFs), remains an active and important area in supramolecular chemistry and material science due to their intriguing structural diversities and interesting properties in gas storage, magnetism, photoluminescence, and catalysis [1 – 4]. A large number of such materials with predictable structures have been constructed by various strategies [5]. The strategy for constructing MOFs mainly depends on the selection of metal ions and organic ligands. As for the organic bridging ligands, aromatic polycarboxylic acids, especially 1,4-benzenedicarboxylic acid ($1,4-H_2BDC$), are widely used as bridging spacers for fabricating coordination polymers with robust network structures and interesting properties. In this area, some of the most spectacular results have arisen from Yaghi's group [6 – 10]. Benchmark examples demonstrating the coordination chemistry of Zn(II) ion with 1,4-benzenedicarboxylate (BDC) have been reported, where the 2D $\{[Zn(BDC)(H_2O)] (DMF)\}_n$ (termed MOF-2) [6] and 3D $\{[Zn_4(\mu_4\text{-}O)(BDC)_3] (DEF)\}_n$ (termed MOF-5) [7] were achieved. However, few documents have been concerned with the self-assembly of polymeric Zn(II)-carboxylate systems based on substituted BDC derivatives so far [11 – 14]. Notably, the known results show that the presence of bulky *ortho* substituents on the BDC-type ligands can significantly affect the relative orientation of the carboxylate groups to give different binding modes upon complexation of Zn(II) ions owing to steric hindrance. Recently, BDC-type ligands modified by the halogen substituents fluorine [15], chlorine [16], bromine [17], and iodine [18] have been documented. Burrows reported the assembly of 3D mixed-component zinc(II)-organic frameworks through control of the incorporation of brominated and iodinated terephthalates providing opportunities to tailor the composition and function of MOFs [19]. Lin and co-workers presented 1D Zn(II) coordination polymers with 2,3,5,6-tetraiodo-1,4-benzenedicarboxylate, which was applied for nanoparticle materials used for computed tomography (CT) contrast enhancement [18]. Very recently, Chen and co-workers reported the assembly of 1D Zn(II) tetrafluoroterephthalate coordination networks in different solvent systems [20 – 22]. To further evaluate the role of such iodine functionality, herein, we used 2,5-diiodo-1,4-benzenedicarboxylic acid (H_2BDC-I_2) as the building

block, and obtained a new 2D dinuclear Zn(II)-organic framework $[Zn(BDC-I_2)(DMF)]_n$ (**1**). Herein, we wish to report the synthesis, structural characterization, thermal stability and solid-state luminescence properties of **1**.

Results and Discussion

Synthesis and general characterization

Solvothermal synthesis has been extensively used for the preparation of coordination compounds as 1D, 2D and 3D systems. In this case, we have successfully used solvothermal synthesis in Teflon autoclaves under autogeneous pressure to obtain compound **1** by reacting $Zn(NO_3)_2 \cdot 6H_2O$ with H_2BDC-I_2 in a mixed solvent system (DMF-ethanol). When $Zn(OAc)_2$ and $Zn(ClO_4)_2$ were used, complex **1** could also be isolated by the same procedure (confirmed by IR spectra and X-ray structure analysis), which suggests that the nature of the final products is independent of the anions under such solvothermal conditions. Complex **1** is air-stable at room temperature and insoluble in water and common organic solvents, which is consistent with its polymeric nature. Slight peak shifts and variations of intensities in the PXRD patterns (Fig. 1) can be attributed to differences in the temperature at which data were acquired and the degree of solvent loss from the sample. In the IR spectrum of **1**, the antisymmetric and symmetric carboxylate stretching vibrations are found in the range of $1590-1640\,\mathrm{cm^{-1}}$ and $1380-1430\,\mathrm{cm^{-1}}$, respectively. The absence of the characteristic band at $\sim 1708\,\mathrm{cm^{-1}}$ for the free H_2BDC-I_2 molecule indicates the complete deprotonation of the carboxyl

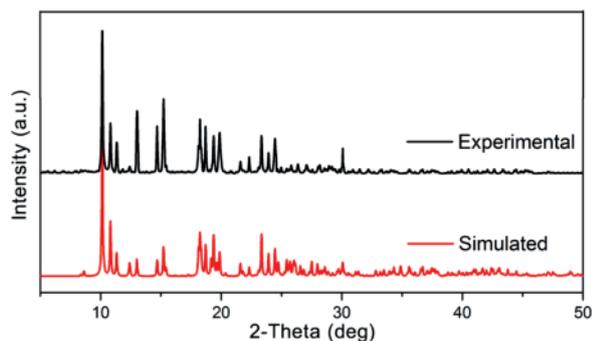groups, which is consistent with the consideration of charge balance.

Description of the crystal structure

Complex **1** crystallizes in the monoclinic space group *C*2/*c*, and the asymmetric unit consists of one Zn(II) ion, one BDC-I_2 dianion and one DMF ligand. Each Zn(II) ion is in a slightly distorted square-pyramidal coordination environment, coordinated by
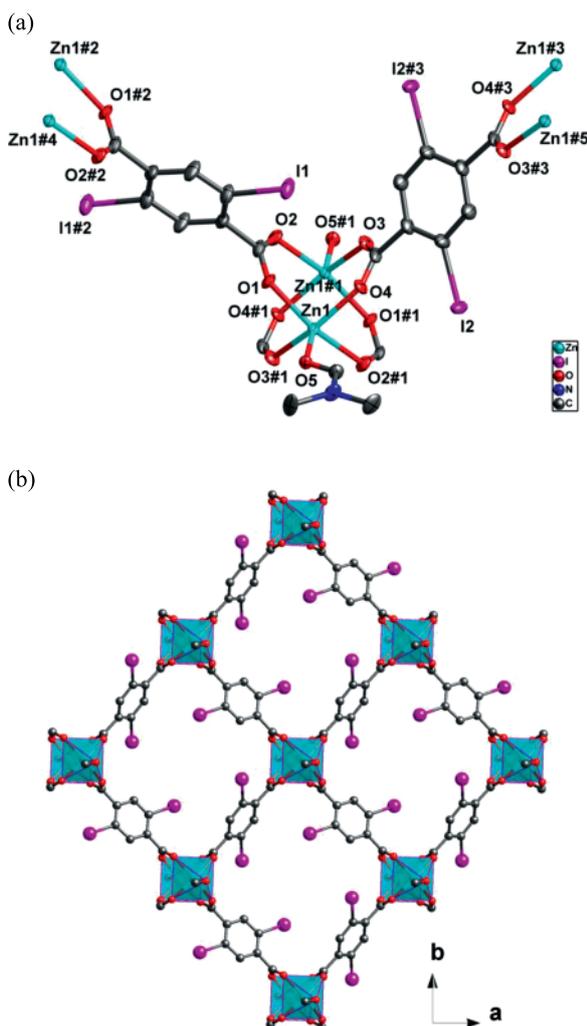
(a)

(b)

Fig. 2 (color online). View of (a) the molecular structure of the dinuclear coordination unit of **1** (symmetry codes: #1 $-x+1/2, -y+1/2, -z$; #2 $-x+1, -y+1, -z$; #3 $-x, -y, -z$; #4 $x+1/2, y+1/2, z$; #5 $x-1/2, y-1/2, z$) and (b) the layer structure of **1** parallel to the crystallographic *ab* plane.

Fig. 1 (color online). Experimental and simulated PXRD patterns for complex **1**.

four oxygen atoms from four BDC-I$_2$ ligands in the basal plane, and one oxygen atom from one DMF ligand at the apex (Fig. 2a). The Zn–O bond lengths vary from 1.988(4) to 2.060(3) Å, and the O–Zn–O bond angles range from 86.7(1) to 159.4(1)°. Notably, owing to the steric hindrance of the bulky iodine atoms located at the *ortho* positions, the dihedral angles between the carboxylate groups and the benzene ring are 44.8(1) and 71.9(2)°, respectively, which is obviously smaller than that observed in Zn(II) complexes with tetraiodoterephthalate [18, 20 – 22]. Each BDC-I$_2$ dianion bridges four Zn(II) ions with the two carboxylate groups adopting a familiar bridging bis-bidentate mode, where the Zn···Zn distance of 2.981(1) Å is typical for carboxylate-bridged dinuclear Zn(II) species constructed from BDC-type ligands [19, 23]. As a result, pairs of Zn(II) ions are bridged by four carboxylates to form dinuclear secondary building units (SBUs), of which a 2D (4,4) coordination network parallel to the *ab* plane is composed (Fig. 2b), containing a nearly square grid with a size of 10.926×10.925 Å^2. The coordinated DMF molecules are anchored on both sides of the 2D coordination motif. Between these neighboring layers, there exist weak C11–H11B···I1^i interactions (H···I/C···I distance: 3.324/4.111 Å, angle: 140.5°, i $= -x + 1/2$, $y + 1/2$, $-z + 1/2$) of the DMF molecules and the iodine atoms of BDC-I$_2$ to realize the final 3D supramolecular architecture.

Thermal stability

To examine the thermal stability of **1**, a thermogravimetric analysis (TGA) of a crystalline sample was performed from room temperature to 800 °C. The corresponding curve is depicted in Fig. 3. It shows the first weight loss of 12.9 % (calculated: 13.2 %), occurring from 105 to 200 °C, corresponding to the release of coordinated DMF molecules. Pyrolysis of the remaining framework starts at 250 °C, which continues up to *ca.* 700 °C. The final solid has a weight of 14.7 % of the total sample, which is close to that of ZnO (calculated: 14.6 %).

Photoluminescence properties

Taking into account the excellent luminescence properties of many other Zn(II) (d^{10}) complexes, the photoluminescence of **1** and of the organic ligand H$_2$BDC-I$_2$ in the solid state was investigated at room
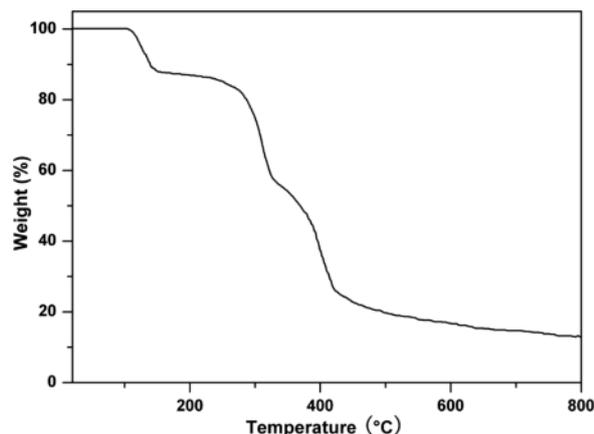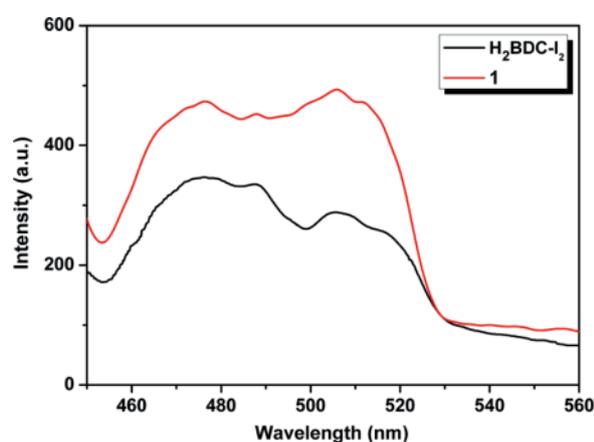

Fig. 3. TGA curve of complex **1**.

Fig. 4 (color online). Solid-state fluorescence emission spectra of complex **1** and the free ligand H$_2$BDC-I$_2$.

temperature (Fig. 4). Upon excitation at 338 nm, the free ligand exhibits fluorescent emission maxima at 476 and 507 nm, which can be ascribed to $\pi \rightarrow \pi^*$ and/or n $\rightarrow \pi^*$ transitions. For **1**, emission maxima are similarly observed at 477 and 507 nm, respectively, which can also be assigned to ligand-centered transitions.

Conclusion

In summary, solvothermal synthesis has produced a new Zn(II) coordination polymer with the iodinated terephthalate ligand BDC-I$_2$, which was structurally characterized. In virtue of the bridging role of carboxylate, two adjacent Zn(II) ions are combined to consti-

tute a dinuclear $Zn_2(CO_2)_4$ SBU, and each SBU is further extended by the backbones of the BDC-I_2 spacers to result in a layer structure. Interlayer C–H···I interactions are found to stabilize the final 3D supramolecular architecture. Further efforts to design and prepare novel coordination frameworks with various iodinated benzenedicarboxylates are made in our laboratory.

Experimental Section

All chemicals were reagent grade as obtained from commercial sources and used as received without further purification. The Fourier transform (FT) IR spectra using KBr pellets were recorded on a Nicolet ESP 460 FT-IR spectrometer. Elemental analyses were performed on a PE-2400II (Perkin-Elmer) analyzer. Thermogravimetric analysis (TGA) experiments were carried out on a Dupont thermal analyzer from room temperature to 800 °C (heating rate: 10 °C min^{-1}, nitrogen stream). Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/max-2500 diffractometer at 40 kV and 100 mA for a Cu target tube ($\lambda = 1.5406$ Å). The calculated PXRD patterns were obtained from the single-crystal diffraction data using the PLATON software [24, 25]. Solid-state fluorescence spectra were measured at room temperature on a Varian Cary Eclipse spectrometer.

Synthesis of [Zn(BDC-I$_2$)(DMF)]$_n$ (1)

A mixture of H$_2$BDC-I$_2$ (43 mg, 0.2 mmol) and Zn(NO$_3$)$_2$ · 6H$_2$O (29.7 mg, 0.10 mmol) in 8 mL of a DMF-ethanol (v/v: = 1 : 1) mixed solvent was sealed in a Teflon-lined stainless-steel autoclave and heated at 85 °C under autogeneous pressure for 48 h, and then cooled to room temperature. Colorless block-shaped crystals were collected and washed with DMF, ethanol and ether. Yield: 40 % based on H$_2$BDC-I$_2$. – Anal. for C$_{11}$H$_9$I$_2$NO$_5$Zn (%): calcd. C 23.83, H 1.64, N 2.53; found C 23.27, H 1.68, N 2.41. – IR (cm^{-1}, KBr pellet): $\nu = 3425$ (br), 2931 (m), 1632 (s), 1486 (s), 1432 (m), 1385 (s), 1337 (s), 1267 (s), 1112 (m), 1083 (s), 1026 (s), 825 (m), 792 (m), 747 (s), 673 (m).

X-Ray structure determination

The single-crystal X-ray diffraction measurement was performed on a Bruker Apex II CCD diffractometer at ambient temperature with MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction was applied using SADABS [26], and the program SAINT [27] was used for integration of the diffraction profiles. The structure was solved by Direct Methods using SHELXS of the SHELXTL package and refined anisotropically for all non-H atoms by full-matrix least squares on F^2 with SHELXL [28, 29].

Although there were eight peaks in the Fourier difference map within the voids of the crystal structure, these highly disordered solvent molecules were not crystallographically well defined. Consequently, the SQUEEZE routine of PLATON [24, 25] was used in order to eliminate the contribu-

Table 1. Crystal structure data for **1**.

	1
Empirical formula	C$_{11}$H$_9$I$_2$NO$_5$Zn
M_r	554.36
Crystal size, mm^3	$0.18 \times 0.17 \times 0.15$
Crystal system	monoclinic
Space group	$C2/c$
a, Å	15.288(2)
b, Å	15.615(2)
c, Å	18.563(4)
β, deg	109.969(5)
V, Å^3	4165.0(1)
Z	8
$D_{calcd.}$, g cm^{-3}	1.77
μ(MoK$_\alpha$), cm^{-1}	4.1
$F(000)$, e	2064
hkl range	$\pm 18, \pm 18, -22 \rightarrow +17$
Refl. measured/unique/R_{int}	11 218/3630/0.0477
Param. refined	183
$R^a/R_w{}^b$	0.0366/0.0984
GoF (F^2)^c	1.069
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.92/−1.23

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; ^{c} GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses^a.

Distances	
Zn1–O1	2.035(3)
Zn1–O2	2.060(3)
Zn1–O3	2.012(3)
Zn1–O4	2.045(3)
Zn1–O5	1.988(4)
Zn1–Zn1#1	2.981(1)
Angles	
O1–Zn1–O2	159.4(2)
O1–Zn1–O3	88.5(2)
O1–Zn1–O4	88.9(2)
O1–Zn1–O5	100.4(2)
O2–Zn1–O3	88.2(2)
O2–Zn1–O4	86.7(2)
O2–Zn1–O5	100.2(2)
O3–Zn1–O4	158.6(2)
O3–Zn1–O5	103.1(2)
O4–Zn1–O5	98.3(2)

^{a} Symmetry code: #1: $-x + 1/2, -y + 1/2, -z$.

tion of disordered solvent molecules. In general, hydrogen atoms were located geometrically and allowed to ride during the subsequent refinement. Further crystallographic data and structural refinement parameters are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC 879560 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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